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HALOCARBON PRODUCTION FROM OXIDATIVE BIOCIDES IN ESTUARINE WATERS

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A large sewage treatment plant served as a volatile halocarbon source to study the fate of these compounds. The major loss mechanism appears to be volatilization to the atmosphere. Rates for this process are estimated. However, there appears to be some loss under winter ~~ince~~ ice cover, perhaps because of chemical or biological degradation.

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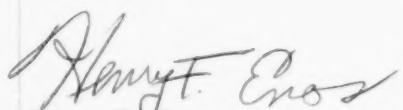
FOREWORD

The protection of our estuarine and coastal areas from damage caused by toxic organic pollutants requires that regulations restricting the introduction of these compounds into the environment be formulated on a sound scientific basis. Accurate information describing dose-response relationships for organisms and ecosystems under varying conditions is required. The Environmental Research Laboratory, Gulf Breeze, contributes to this information through research programs aimed at determining:

- the effects of toxic organic pollutants on individual species and communities of organisms;
- the effects of toxic organics on ecosystem processes and components;
- the significance of chemical carcinogens in the estuarine and marine environments.

The production and fate of halo-organic compounds that are by-products of disinfection/biofouling control processes are investigated in the research project described in this report.



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ABSTRACT

The formation of halo-organic compounds by chlorination of estuarine waters has been investigated under both laboratory and field conditions. Haloforms are readily generated in the laboratory with chlorine doses of 1 to 10 mg/l, the range employed by many coastal power plants. At salinities above 1 g/kg (i.e., one part per thousand), Br is the principal halogen in the haloform products. On a molar basis, more than 4% of the chlorine was converted to haloforms in some tests. In the laboratory, ozone also generated haloforms in estuarine water; the yields were similar to those obtained from chlorine. However, only traces of haloforms were found at a power plant field site, where haloform-bypassing reactions apparently consume free chlorine much faster than in the laboratory. Identification of these reactions is uncertain, but they may involve formation of stable halogenated macromolecules.

A large sewage treatment plant served as a volatile halocarbon source to study the fate of these compounds. The major loss mechanism appears to be volatilization to the atmosphere. Rates for this process are estimated. However, there appears to be some loss under winter ice cover, perhaps because of chemical or biological degradation.

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SECTION 1

INTRODUCTION

Chlorine is injected directly into marine waters by large coastal power plants that use chlorine to prevent biofouling of their heat exchangers. Chlorinated effluents are also injected into marine waters by wastewater treatment plants and certain industrial enterprises. Since the discoveries of haloforms in chlorinated drinking waters by Rook (1976) and a number of halo-organics in chlorinated sewage treatment plant effluents by Jolley (1974), there has been concern about whether such compounds adversely affect aquatic environments because large volumes of chlorinated discharges are entering coastal environments. For example, in the northern Chesapeake Bay, 2% of the non-saline throughput is now treated wastewater effluent (Brush, 1972). Based on past rates of growth, this fraction will reach 30% or more in another century. Power plants currently circulate a volume greater than 10% of the non-saline throughput; if past technology and trends continue, a volume approaching this throughput will be circulated by the end of this century (Bongers, 1973). It is likely that similar statistics could be cited for many other major estuaries. Thus, any persistent, bioactive compound injected into the aquatic environment from these sources may be capable, in principle, of producing massive alterations in our coastal waters.

When this project began, no previous work had been done on the formation of halo-organics through chlorination in marine waters. Yet there was substantial evidence that the behavior of chlorine in marine waters differs from its behavior in fresh waters because of the involvement of Br^- (which is ubiquitous in seasalt) in the halogen chemistry. Similarly, some differences were known to exist between the organic matter in marine and fresh water systems. Thus, research on halo-organic formation in marine waters seemed warranted. A distinctive feature of this project is the inclusion of a major field study to explore the production and fate of halocarbons in the natural environment.

SECTION 2

CONCLUSIONS

1. Trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$) were generated at the 10 to 1000 μM (~3 to 300 ppb) level when fluvial and estuarine water samples were chlorinated under laboratory conditions.

2. When salinity exceeded 5 g/kg (‰) bromoform was virtually the only trihalomethane product.

3. No volatile halocarbons other than trihalomethanes in estuarine water of 14 g/kg salinity were found at the μM level by headspace analysis.

4. When both ozone and chlorine were applied in estuarine water of 14 g/kg salinity to produce after 10 minutes a residual of 22 μequiv/liter (0.78 ppm as chlorine), they produced identical trihalomethene yields.

5. Field studies at an estuarine power plant that employs continuous chlorination revealed only traces (~1μg/liter) of volatile halocarbon products.

6. No "free chlorine" (as measured amperometrically at pH 7) was observed beyond the condensers at this plant, and the negligible yields of trihalomethanes are tentatively ascribed to the extremely rapid consumption of free chlorine in the condensers. More work should be done to test this hypothesis.

7. It was possible to trace the halocarbon plume from a wastewater treatment plant more than 5 miles seaward under winter ice, but only a fraction of this distance in spring when the ice was gone.

SECTION 3

LABORATORY EXPERIMENTS ON VOLATILE HALOCARBON PRODUCTION

Haloforms, the most abundant known halo-organic products from chlorination of freshwaters, were a major concern in this project. In this section, we describe our analytical method and provide some basic experimental data on the nature of the haloforms produced by chlorinating estuarine waters.

ANALYTICAL METHOD FOR VOLATILE HALOCARBONS

In the field, 40.0 ml of sample was placed in a Hypovial (nominal size 50 ml; actual volume when sealed as described, 60.19 $\pm$ 0.72 ml; Pierce Chemical Co.). If oxidant was present, it was quenched with a drop of concentrated $Na_2S_2O_3$ solution. Then, a Teflon-to-rubber laminated septum was placed over the mouth and sealed in place with a crimped aluminum ring. The sample was stored on ice and normally analyzed within 48 hours. In laboratory chlorination studies, the samples were first treated with the desired amount of NaOCl and then sealed as above. For analysis, the vials were equilibrated at 60°C in a shaking water bath; 1 ml of the vapor was extracted through the septum cap with a gas-tight hypodermic syringe, and injected into a gas chromatograph equipped with a Hall Electrolytic Conductivity Detector (Tracor). The following conditions were normally used: carrier gas, 30 ml He min^{-1}; column packing, 60-80 mesh Tenax GC (Applied Science Labs, Inc.); temperature in injection port, 200°, in column, 120°-200° programmed at 8° min^{-1}, in transfer line, 250°, in detector furnance, 850°; detector reaction gas, 50 ml H_2 min^{-1}; detector electrolyte, 50% n-propanol-water. Standards were prepared in distilled water using aliquots of a primary standard that contained 1 gram each of the compounds of interest, then brought to 100 ml with methanol. Coefficients of variation, based on repeated analysis of standards in the 10^2 to 10^3 nM range, were about 4%. In early stages of the work, some identifications were checked by mass spectrometry, but the high selectivity of the method for volatile chloro- and bromocarbons minimizes the danger of misidentifying gas chromatograph peaks.

When saline samples are analyzed, using a standard curve prepared from solutions of the analyte in distilled water, the apparent concentration C_A, obtained from the standard curve must be corrected for salting out in the sample. If C_T and C_A are the true and apparent original concentrations of a compound in the test solution, V_V and V_L are the volumes of vapor and liquid, H_T is the Henry's Law constant expressed as a concentration ratio, S is the salinity, and σ is the Setchenow coefficient of the compound in water, then the relationship between the true and apparent concentration is:

$$C_T = \left[\frac{e^{-\sigma S} + \frac{H_T V_V}{V_L}}{1 + \frac{H_T V_V}{V_L}} \right] \times C_A \qquad (1)$$

For the haloforms, H_{60} is 0.45, 0.25, 0.17 and 0.02 for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$, respectively. A reasonable numerical value for σ is 0.008 when salinity is expressed in g/kg. Using these figures in Equation (1), we found that C_T is less than C_A in 35 g/kg seawater by about 25% for $CHCl_3$ and by about 30% for $CHBr_3$. The correction factor diminishes with salinity, and is within the range of analytical uncertainty for salinities below about 5 g/kg.

Our headspace method provides a measure of the amount of analyte that is free and unassociated with molecules other than water. If part of the analyte is adsorbed or bound in some non-volatile form, that fraction will go effectively undetected. Table 1 presents some data on potential adsorbing agents. These were added at concentrations higher than would be

TABLE 1. CONCENTRATION (µg/l) OF 100 µg/l HALOFORM SOLUTIONS ONE DAY AFTER ADDITION OF ADSORBING AGENTS

Haloform	Adsorbing Agent		
	Humic Acid (a)	$Fe(OH)_3$ (b)	Clay (c)
$CHCl_3$	98	101	99
$CHBrCl_2$	99	93	96
$CHBr_2Cl$	101	93	95
$CHBr_3$	100	89	92

a. Aldrich Chem. Co. lot no. 121137; 10 mg/l.
b. Precipitated from $FeCl_3$ and aged 1 hr before exposure to haloforms; 10 mg/l.
c. Wyoming Na-Montmorillonite, Clay Minerals Repository, University of Missouri; 20 µg/l.

encountered typically in coastal waters. Inasmuch as the measurement uncertainty is about 4%, the data for humic acid do not show significant absorption. In the presence of $Fe(OH)_3$ and montmorillonite, there is significant absorption for the heavier haloforms. However, in most estuarine and marine waters where the concentrations of these adsorbing agents would be many times less, the small effects seen in Table 1 would

become negligible. Thus, we conclude that volatile halocarbons are likely to be mainly in a free state in natural waters; therefore, concentrations obtained by a headspace procedure, when corrected by Equation 1, approximate total concentrations.

In concluding this section, it should be noted that Kopfler et al. (1976) and Nicholson et al. (1977) have provided evidence for the existence of a long-lived halo-organic intermediate in chlorinated natural waters that decays to release haloforms upon heating. Thus, in the case of decay of such an intermediate, the quantity of haloforms detected by our technique may be greater than the quantity in the sample at the time it was collected.

LABORATORY CHLORINATION EXPERIMENTS

Sampling Sites

To study halocarbon production by chlorination of coastal waters, a group of seven samples was collected from coastal, estuarine and fluvial sites in Maryland (Figure 1). The sites were selected to avoid local sources of either haloforms or chlorine. The samples were filtered with 0.45 μm

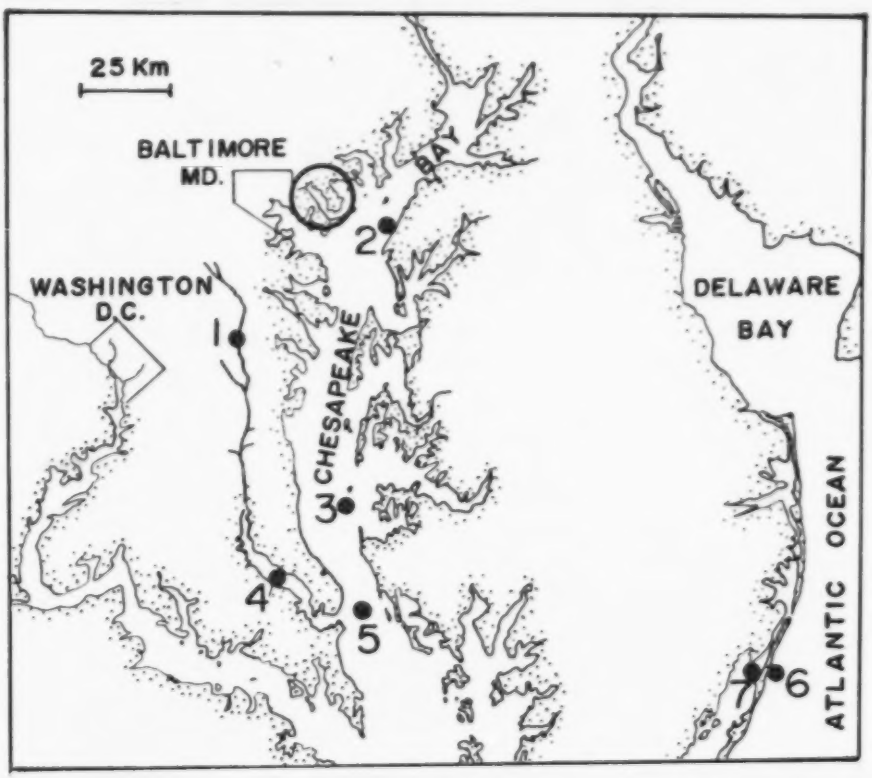


Figure 1. Map showing sample locations. See Appendix for latitude and longitude.

Millipore filters, and then stored in a cold room (4°C) prior to use in experiments. Chlorination in the laboratory was conducted with calibrated NaOCl stock solutions, rather than with Cl_2 gas; under the conditions of the tests, Cl_2 hydrolyzes almost instantly to form OCl^-, so our results should be the same as would be obtained with Cl_2. Total nitrogen data for these samples were obtained by a UV oxidation-Cd reduction method (Sugam, 1977). Total organic carbon determinations were done by a commercial laboratory (Martel Laboratories, Inc.), using an Oceanography International organic carbon analyzer.

Results

Table 2 presents the results of a series of chlorination experiments in which samples selected to represent a full range of water conditions, from fresh water to ocean water, were treated with two concentrations of NaOCl in

TABLE 2. HALOFORMS PRODUCED IN SELECTED ESTUARINE AND COASTAL WATER SAMPLES (10^{-9} moles/l)[a]

	Sample Number						
	1	2	3	4	5	6	7
Salinity (g/kg)	0.00	1.06	3.68	7.90	10.27	30.35	31.54
pH	7.21	7.94	7.94	7.83	7.82	7.86	8.10
Org-C (μM)	350	270	270	280	270	240	510
Tot-N (μM)[b]	185	68	58	34	31	13	NA[c]
NaOCl dose 14 μM (=1 mg/l):[d]							
$CHCl_3$	20	15	ND	3	ND	ND[c]	NA
$CHBrCl_2$	ND	17	7	1	ND	ND	NA
$CHBr_2Cl$	ND	15	28	13	7	ND	NA
$CHBr_3$	ND	22	183	211	122	54	NA
Yield (%)[e]	0.43	1.48	4.67	4.88	2.76	1.15	-
Cl Demand (%)[f]	18	22	74	78	77	55	NA
NaOCl dose 140 μM (=10 mg/l):							
$CHCl_3$	763	41	10	4	8	6	ND
$CHBrCl_2$	287	163	11	3	1	ND	ND
$CHBr_2Cl$	87	564	126	42	27	9	16
$CHBr_3$	ND	753	970	1160	900	245	880
Yield (%)	2.43	3.25	2.39	2.59	2.00	0.56	1.92

a. All data are based on a single analysis for each parameter in each sample.
b. Tot-N = NO_3^- + NO_2^- + NH_3 + Org-N.
c. NA = not analyzed; ND = not detected.
d. 1 μM NaOCl has the same oxidizing capacity as 1 μM Cl_2.
e. Yield = moles of halogen in haloforms as percent of moles of hypochlorite added. Note that carbon is in excess in these tests.
f. Cl Demand = percentage of initial dose detectable after 10 min by amperometric titration at pH 4.0 with excess KI added.

the laboratory. These levels span the range of doses typically applied by power plants and treatment plants. Haloforms were produced in each case; no volatile halocarbons other than haloforms were produced at the nM level in any of the experiments. In the fresh water sample (No. 1), $CHCl_3$ was the dominant haloform, as has been found in most drinking waters. Conversely, $CHBr_3$ overwhelmingly dominated in the ocean samples. There was a systematic shift, as the salinity increased (i.e., left to right in Table 1), in the proportion of bromine present in the haloform products. Figure 2 shows that bromine dominated the products at salinities above about 5 g/kg.

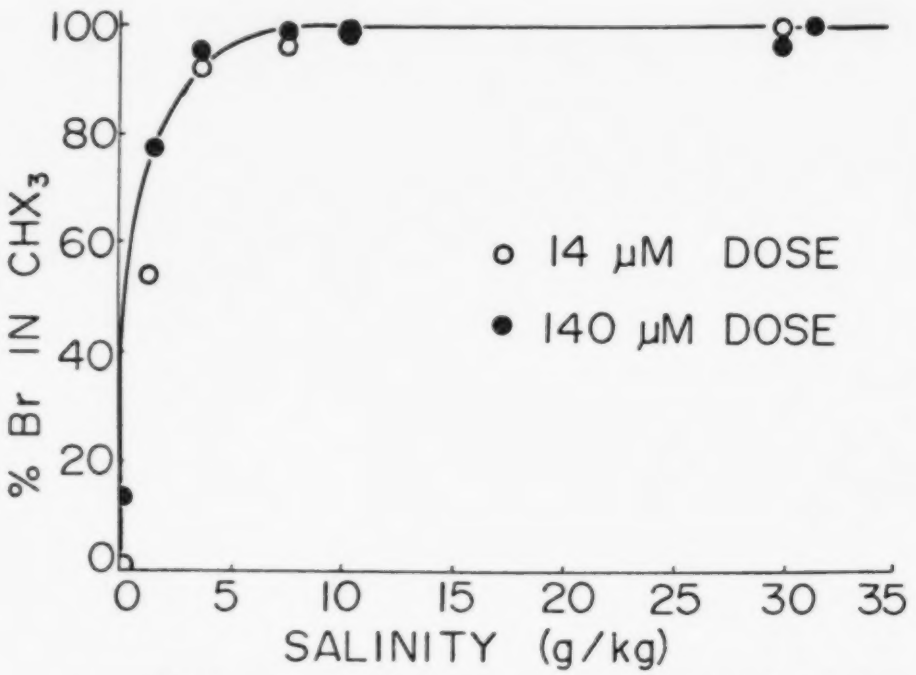


Figure 2. Bromine as a percentage of total halogen in haloform products.

The total haloform yield, expressed as a percentage of the chlorine dose (i.e., the amount added initially), varied considerably (Figure 3), but generally seemed to be higher at low-to-intermediate salinities. Absolute haloform yields were roughly proportional to chlorine dose, so that percentage yields were of similar magnitude for both dosages tested. Although on a molar basis, organic carbon greatly exceeded chlorine dosage in both sets of tests, its availability appeared nevertheless to exert some minor influence on yield. (Samples 6 and 7 are very similar, except for organic carbon content; sample 7, with higher organic carbon, yielded much more haloform).

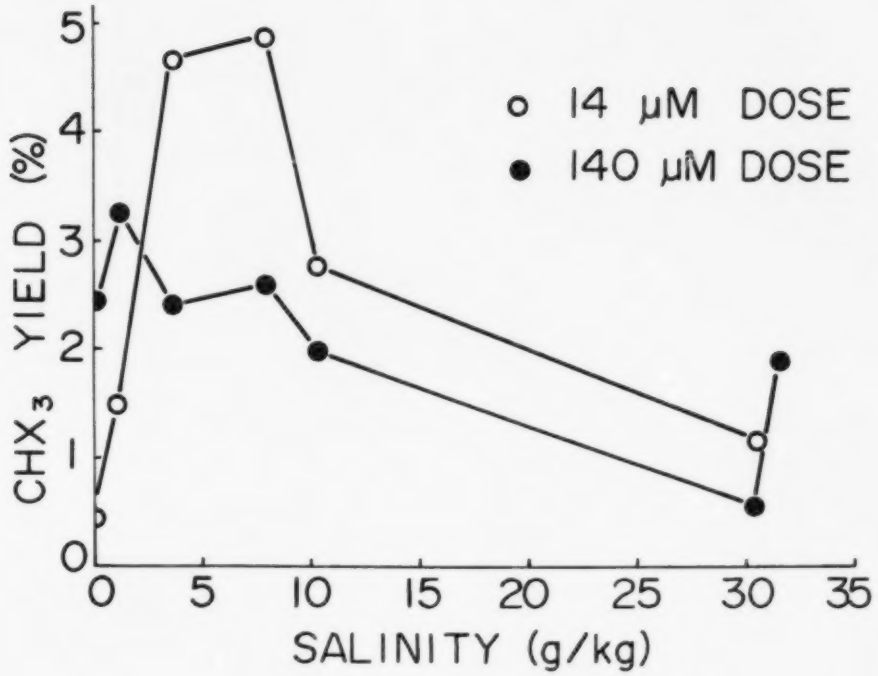


Figure 3. Total haloform yield as a percentage of chlorine dose; chlorine added as NaOCl.

It is particularly interesting to note (Figure 4) the correlation between the percentage of the chlorine dose that disappeared within 10 minutes and the yield of haloforms produced. This suggests that organic matter plays a major role in chlorine consumption, even though only a small fraction of the consumed chlorine is recovered in the form of volatile halocarbons.

Discussion

When chlorine is added to seawater, bromide which is present at a concentration of about 840 μM is rapidly oxidized to HOBr (e.g. Duursma and Parsi, 1976; Eppley et al., 1976):

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (2)$$

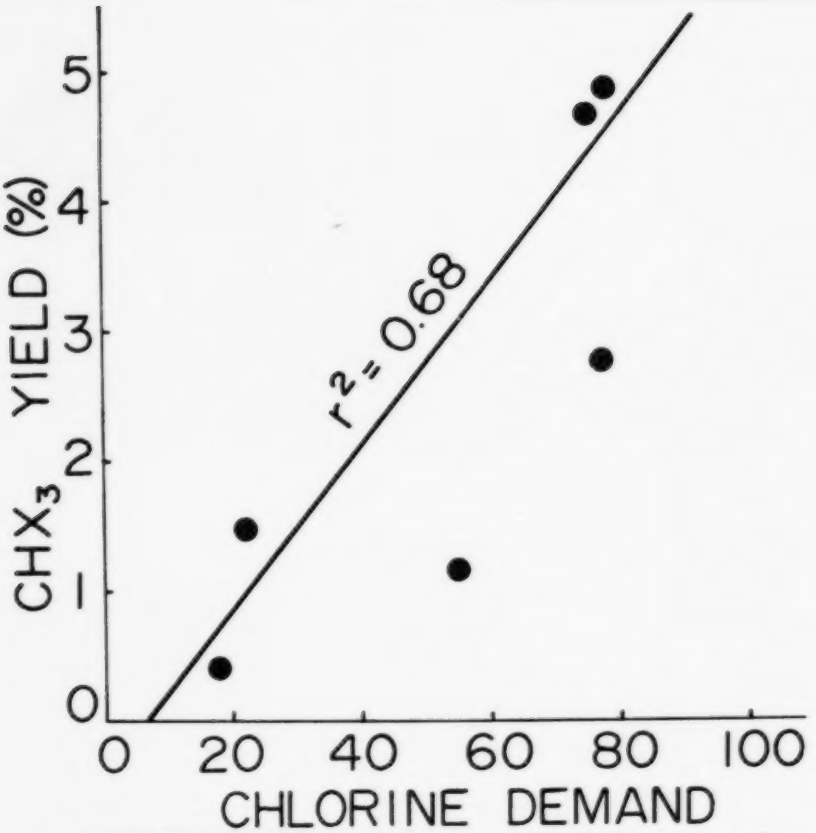


Figure 4. Haloform yield as a percentage of chlorine dose vs. total chlorine consumed in 10 min, as a percentage of chlorine dose; dose was 14 μM.

Using the ionization constant data of Sugam and Helz (1976) and the rate constant data of Farkas et al. (1949), we calculated the time needed for HOCl to be consumed by reaction 2 (see Figure 5). It was assumed in these calculations that the chlorine dose was small compared to the available Br^- so chlorine consumption could indeed reach 99% completion. For typical doses, this assumption must break down at low salinities. Also at pH of 9 and higher, equilibrium between OCl^- and OBr^- is reached before 99% of the hypochlorite has been consumed. Nevertheless, the figure clearly shows that under near-neutral conditions at salinities above about 5 g/kg, consumption of HOCl by Br^- will occur within less than 1 min; in many cases, the conversion time will actually be less than 10 sec. Thus, the dominance of Br in haloform products formed in waters that contain more than 5 g/kg seasalt is readily explained. As pointed out in a later section, these results imply that the organic substitution reactions which give rise to haloforms are slow compared to reaction 2.

The fact that haloforms are the only major volatile halocarbon product of the direct chlorination of marine waters (as with drinking waters) implies that a unique mechanism exists for their synthesis. Recently, Rook (1977) suggested that halogen attack begins at the 2nd carbon position in a 1,3-

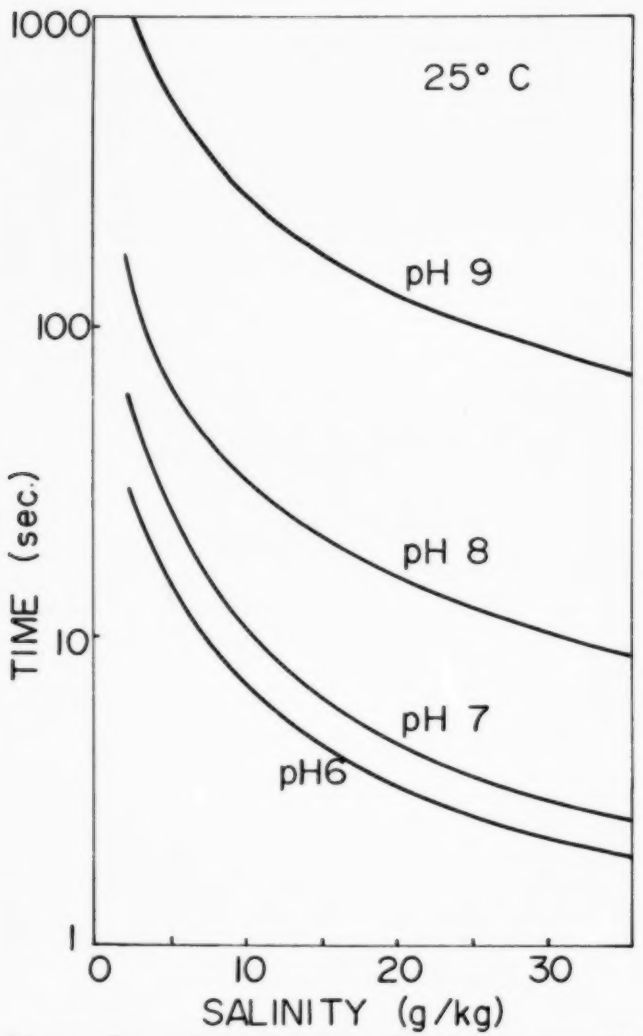


Figure 5. Calculated time for 99% consumption of free chlorine by reaction 2 (see text).

dihydroxybenzene (resorcinol)-type unit in fulvic acid, thus leading to ring cleavage and release of a haloform molecule. In freshwaters, 60-80% of the dissolved and particulate organic carbon typically consists of humic substances, including fulvic acid (Reuter and Perdue, 1977). Although a number of workers have pointed out differences between organic matter in freshwater and seawater (Kalle, 1966; Khaylov, 1968; Sieburth and Jensen, 1968; Stuermer and Harvey, 1974; Kerr and Quinn, 1975), sufficient similarity apparently exists, nevertheless, to justify common use of the term, fulvic acid, to describe marine dissolved-organic matter. Our results indicate that fluvial and marine organic matter share the ability to produce haloforms.

It is clear from these and other results (Rook, 1974) that the organic matter that supplies carbon for the haloforms reacts preferentially with Br, rather than Cl. For example, sample 3 which contained 86 μM Br^- (estimated from salinity) could have consumed a maximum of only about 60% of the 140 μM chlorine dose via reaction 2. Yet the excess chlorine is scarcely represented in the haloform products (Table 2).

One likely reason why chlorine in haloforms is disproportionately low is that reactions involving ammonia, organic amines and amino acids rapidly tie up chlorine in chloramine compounds:

$$HOCl + R\text{-}NH_2 \rightarrow R\text{-}NHCl + H_2O \qquad (3)$$

$$HOCl + R\text{-}NHCl \rightarrow R\text{-}NCl_2 + H_2O$$

These reactions are extremely fast (Morris, 1967). The products are oxidants, but probably cannot react with dissolved organic matter to produce haloforms. Analogous bromamines also can form in marine waters, but, at least in the case of the inorganic bromamines, their formation is reversible (Johnson and Overby, 1971). Thus, chlorine that becomes nitrogen-bound may be permanently removed from the haloform generation process, whereas nitrogen-bound bromine may continue to be available.

COMPARISON OF CHLORINATION AND OZONATION OF ESTUARINE WATER

A few exploratory experiments were conducted in cooperation with Dr. Ronald Block, of the Chesapeake Biological Laboratory, to compare the haloform-generating performance of chlorine and ozone. Those experiments employed his bioassay system and natural estuarine water.

Methods and Results

Data on the water chemistry are given in Table 3. Chlorinated, ozonated, and untreated control solutions were examined in parallel experiments run simultaneously to insure that prior to treatment the water quality was the same. For the chlorine experiments, $Ca(OCl)_2$ stock solution (10.6 equiv/l) was metered at 0.5 ml/min into a 3.8 l/min stream of estuarine water that flowed continuously through an 80-l glass tank; thus, the dosage was 139 μequiv/l, or about 5 ppm Cl. Turnover time of water in this tank was roughly 20 min. The system was allowed to run for several hours until a steady-state level of oxidant in the tank was observed. Then, a sample was collected in a glass bottle and sealed so that no air-space remained in the bottle.

A second sample was obtained at the same time, but dechlorinated with $Na_2S_2O_3$ before sealing. Next, a dozen white perch (Morone americana) were introduced into the tank; after 30 min, two additional water samples (one of which was quenched with $Na_2S_2O_3$) were taken and sealed. In the ozone experiments, the above procedure was conducted in a similar fashion, except that the flowing water was treated with the oxygen-ozone gas effluent from a Welsbach T-816 ozonator; dose was adjusted to give approximately the same

oxidant level as in the chlorine testing tank. Turnover time of water in the ozone tank was 8 min. With the controls, all procedures were followed (i.e. taking of a quenched and an unquenched sample and testing both in the presence and absence of fish). The samples were analyzed for volatile haloorganics 18-24 hours after collection by transferring them to septum vials and then following the method described previously.

Results

As shown in Table 3, bromoform concentrations in the neighborhood of 20 µg/l were found in all the samples that had been treated with hypochlorite or ozone. Furthermore, bromoform was not detectable in the controls. This indicates that bromoform is produced by the oxidants and is not introduced by sample handling or contamination.

TABLE 3. YIELDS OF BROMOFORM IN ESTUARINE WATER* TREATED WITH CHLORINE (AS OCl^-) AND OZONE.

	Fish Absent	Fish Present
Hypochlorite (µ-equiv/l)	23.8	21.2
Bromoform Yield (µg/l)		
$Na_2S_2O_3$ Quench	24.2	20.1
No Quench	25.8	19.8
Ozone (µ-equiv/l)	23.2	21.8
Bromoform Yield (µg/l)		
$Na_2S_2O_3$ Quench	19.0	17.0
No Quench	26.6	19.0
Controls		
$Na_2S_2O_3$ Quench	<1	<1
No Quench	<1	<1

*Chemical characteristics of the water are: salinity = 14 g/kg, pH = 8.0, T = 15°C, NH_3 < 0.1 mg/l, initial dissolved oxygen = 10 mg/l (dissolved oxygen in ozonated tank = 17.7 mg/l). All data are based on a single analysis for each parameter in each sample.

In both the hypochlorite and the ozone tests, introduction of fish lowered the steady-state oxidant concentration and the amount of bromoform observed. In the unquenched samples, the yield of bromoform is essentially the same for both hypochlorite and ozone. Furthermore, in the hypochlorite experiments, quenching with $Na_2S_2O_3$ had little effect upon bromoform yield.

Discussion

The virtually identical haloform yields in the quenched and unquenched chlorine samples indicate that the substitution reactions must be fast compared to turnover time of water in the experimental tank (i.e., 20 minutes, or roughly 1000 seconds) because this is the average time between addition of chlorine and addition of $Na_2S_2O_3$ to the quenched sample. On the other hand, the substitution reactions must be slow compared to reaction

(1) because bromoform is the only significant product. Based on Figure 5, reaction (1) would reach completion in roughly 20 seconds at the salinity and pH of these experiments. Thus, these observations bracket the order of magnitude of the time needed to complete the halogen substitution.

It is important to distinguish between the substitution reactions discussed above and the haloform production reactions. Laboratory studies of haloform production from chlorinated solutions of fulvic or humic acids, believed to be the sources of carbon in the haloforms, suggest that this production requires hours to reach completion (Stevens et al., 1976; Rook, 1976 and 1977). Further, Kopfler et al. (1976) and Nicholson et al. (1977) have provided evidence for the existence of a long-lived halo-organic intermediate that decays to release haloforms upon heating. Thus, the substitution of halogen atoms into organic structures in water, and the release of haloform molecules from those organic structures, appear to be separate processes with quite different rates. The release process apparently does not require the presence of an oxidant residual, implying that in seawater, it would be impossible to limit haloform production by instituting dechlorination practice at power plants unless the entire chlorination-dechlorination cycle can be accomplished in a very short time span.

The excellent agreement in bromoform yield from ozone and chlorine is somewhat surprising. In the case of the unquenched samples, the yield of bromoform is the same within experimental error. For the quenched samples, slightly less bromoform was obtained from ozone than from chlorine, probably reflecting simply the shorter turnover time of water in the ozone-treated tank. It would seem from these data that replacement of chlorine by ozone as an antifoulant in marine power plants offers little advantage for minimizing volatile halo-organics, unless it can be shown that ozone is basically more effective than chlorine and can be used at lower doses.

The chief purpose of placing fish in the test tanks after the first set of samples had been collected was to determine if reaction of the oxidants with excretory products, body, or tissues produced a large increase in the haloform yield or in the Cl/Br ratio in the products. A large enhancement in yield could make haloforms potential toxic factors in bioassay experiments intended to assess the acute toxicity of chlorine and ozone to fish. However, the data indicate small decreases in bromoform content in the tanks when fish are present. A small decline in the residual oxidant is also observed. One possible explanation is that fish produce compounds which react rapidly with oxidative biocides, but which generate no volatile halo-organic compounds. Ammonia, urea, and other nitrogenous products are likely candidates. Probably they compete with the naturally occurring bromoform precursors for the available halogen and thus lower bromoform yield. An alternate hypothesis for the decrease in bromoform may be uptake of this compound by the fish, either through absorption into body slimes or transport into the body via the mouth or gills.

SECTION 4

FIELD STUDIES

This section extends the previous work to the field and includes some evidence regarding the fate of volatile halocarbons in the natural environment.

CHALK POINT POWER PLANT

Site Description

Field work was done at a coal-fired power plant located on the Patuxent River near Benedict, Maryland. Although the upper part of the Patuxent drainage basin contains numerous residential suburbs and has a population density of approximately 500 persons/km^2 (data from Maryland Environmental Service, 1974), the area within 30 km of the plant, both upstream and downstream, is dominantly rural with a population density closer to 50 persons/km^2. The power plant is the only major industrial installation in the lower part of the basin.

The salinity in the vicinity of the plant ranges with season from virtually zero to about 15 g/kg (Cory and Nauman, 1971). Ammonia is typically less than 0.1 mg N/l (Sugam, 1977).

The power plant contains two 355 megawatt generating units that each circulate 16,000 l/sec (560 cfs) of estuarine water through twin single-pass condensers. This water, which is continuously chlorinated, is discharged into a 2.6-km-long cooling canal. At the head of the canal, the condenser effluent is sometimes diluted with unchlorinated estuarine water by as much as a factor of two to meet regulations limiting thermal loading.

Results

A large amount of data was collected on the inorganic aqueous chemistry at this site (mostly under other sponsorship). Data are reported elsewhere (Sugam, 1977) and only will be summarized here. As illustrated by the lower two curves in Figure 6, more than 90% of the oxidant dose disappears by the time the cooling water emerges from the plant. Comparable initial decay has been observed by others (Snoeyink and Markus, 1974; Eppley, 1976; Bongers et al., 1977), but rarely results in loss of as much of the initial dose as we observed at this site. We will refer to this phase of the decay process as the fast phase. At the power plant, it occurs mostly under non-photic conditions inside conduits and condenser plumbing. We could not study this phase in detail because of inadequate access to the water inside the plant.

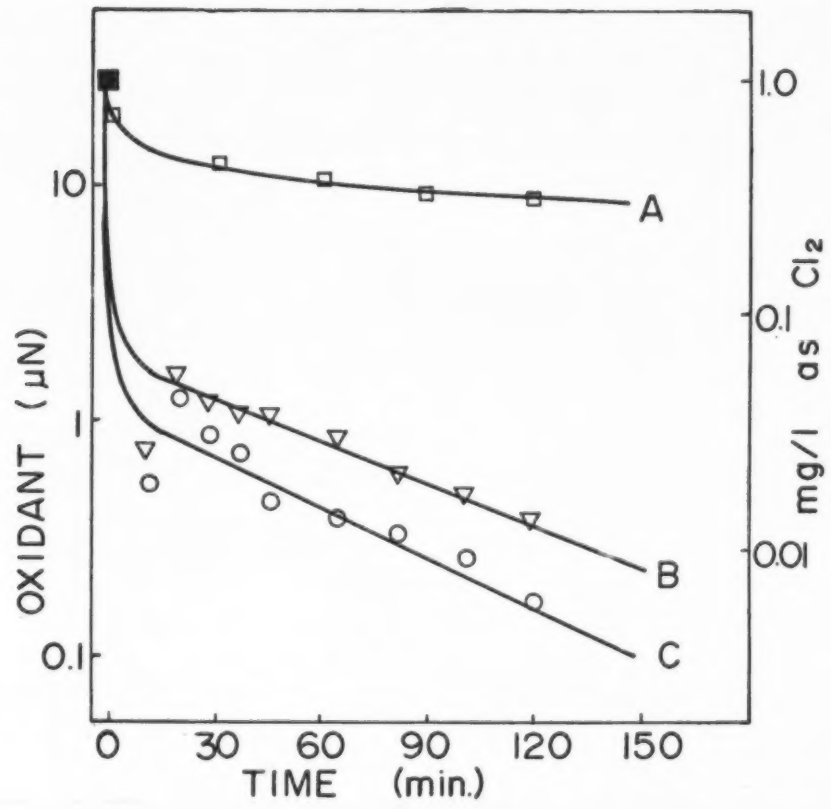


Figure 6. Decay of chlorine-produced oxidants in Patuxent estuarine water. Curve A - intake water chlorinated with NaOCl in the laboratory at room temperature. Curve B - samples collected from discharge canal at night. Curve C - samples collected from discharge canal during the day. Analyses by amperometric titration at pH 4.0 with excess KI.

When samples from the intake canal were chlorinated in the laboratory with doses comparable to those used in the plant (upper curve, Figure 6), the amount of chlorine lost during the fast phase was much less than observed at the power plant canal. Samples extracted from the plumbing upstream of the condensers inside the plant resembled those chlorinated in the laboratory; that is, they did not yet display the large loss of chlorine subsequently observed in the canal.

The fast phase is followed by a slow decay phase. In the discharge canal, this always appeared to be first order in total oxidant concentration with $t_{\frac{1}{2}}$ = 30-100 min. In figure 6, the daytime decay rate appears to be slightly faster than the nighttime decay rate, suggesting that photochemical processes might play a minor role during this phase. However, in other runs, the night decay rates were faster so the general importance of photochemical processes is questionable.

No free chlorine (determined by amperometric procedures) was ever detected in the canal. On the other hand, in laboratory-dosed or precondenser samples, for which the fast decay of total oxidant was much less than in the field, free chlorine persisted for substantial periods of time.

Probably because of the rapid loss of free chlorine, only traces of haloforms (~1 µg/l) were found in discharge canal waters that were collected in gas-tight septum bottles and analyzed 24 to 48 hours later. Yet, 10-100 µg $CHBr_3$/l was readily generated in intake water by chlorinating it with the same dose used by the plant and then processing it as the discharge canal samples were processed. Precondenser samples also yielded haloforms. For example, one sample extracted from the conduit between the chlorine injection point and the condenser inlet was found to contain 40 µg $CHBr_3$/l and traces of $CHBr_2Cl$ when analyzed the next day. However, its total oxidant residual after 1 hr was 11 µN, much higher than that observed in the canal after a comparable period.

Discussion

The finding of only traces of haloforms in the discharge canal at Chalk Point was a very surprising result in view of the ease with which haloforms could be generated under laboratory conditions. Thus, some explanation is required.

One suggestion might be that haloforms actually did form, but were lost (possibly by volatilization) before the water reached the sampling point. In this report, some data are presented on the rates and mechanisms of loss of volatile halocarbons from estuarine waters. These studies suggest no mechanism that could remove halocarbons so rapidly as to result in their absence from the canal only minutes downstream of the plant.

Instead, the negligible haloform yields are probably a consequence of the remarkably rapid oxidant loss in the condensers. This then raises the question, what controls the oxidant loss? Since the fast phase of decay consumed more oxidant within the Chalk Point plant than in experiments that matched the plant's oxidant dose, one might suspect initially that some of the oxidant consumption under the field conditions was caused by reaction with the condensers and plumbing, or with accumulated slimes within them. However, a thorough review of the replacement history of both the condensers and the sacrificial anodes, along with estimates from metallurgical data of the likely corrosion rate of Cu-Ni condensers, suggests that metallic corrosion probably consumes at most only a small percentage of the chlorine used annually. It is also possible to dismiss reduction by slimes or by-products of slime organisms as a major factor with the following argument:

Because this plant chlorinates continuously 5 months a year, biosynthetic production of a hypothetical reducing substance per unit volume of water would have to equal at least the rate of chlorine consumption per unit volume. This exceeds 1 mg Cl_2/l during the ~5 min period that the water is inside the plant. If reductant production did not match oxidant consumption, the store of the reducing substance would be depleted rapidly. Biosynthesis of enough material from each liter of water to accomplish this much reduction is inconceivable in the short time available.

It is more reasonable to argue that the greater fast oxidant consumption observed in the power plant can be explained by thermal and hydrodynamic effects in the water itself. The rate of chlorine decay in estuarine water is strongly temperature-dependent, as seen in Figure 7. Thus, the elevated temperatures in the condensers should enhance decay processes. Further, it

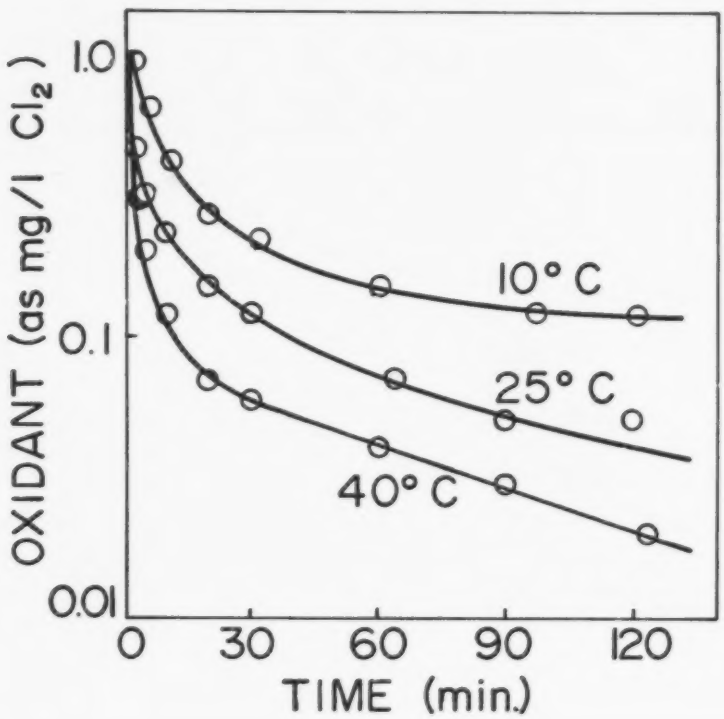


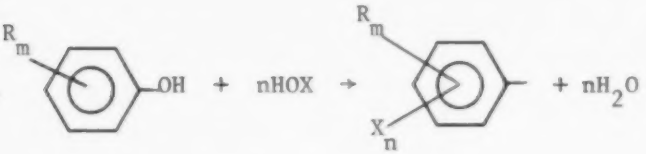
Figure 7. Effect of temperature on decay in estuarine water chlorinated in the laboratory.

will be shown that colloidal organic matter undergoes substitution and deamination reactions with chlorine. It is quite likely that these reactions are partly diffusion-controlled and thus subject to acceleration by the intense agitation occurring inside the condensers.

The search for reducing agents to consume the oxidant probably should be directed toward the water itself. For most well-oxygenated estuarine waters, it is possible to reject common inorganic reducing agents (e.g. Fe^{2+}, Mn^{2+}, S^{2-}, NO_2^-) as major chlorine consumers based upon one or both of the following grounds (Sugam, 1977): either the concentration of the agent in its reduced form is small compared to typical chlorine doses, or available kinetic data suggest that the redox reaction is too slow to explain the large chlorine decay that occurs in the fast phase. The second argument is always subject to the objection that there may be unrecognized catalytic processes occurring under field conditions. Nevertheless, we have come to believe that most chlorine consumption in estuarine waters (especially consumption during the fast phase) must involve reactions mainly of the types listed in Table 4; this list is intended only to provide examples of reaction types, not a definitive list of possible reactions.

TABLE 4: EXAMPLES OF POSSIBLE OXIDANT CONSUMPTION REACTIONS IN ESTUARIES. (X = Cl or Br)

Carbon Reactions (Substitution, Oxidation)

1. 

2. $R-\overset{H}{\underset{|}{C}}=O + HOX \rightarrow R - \overset{OH}{\underset{|}{C}}=O + HX$

3. $R-\overset{H}{\underset{NH_2}{\underset{|}{C}}}-COOH + HOX \rightarrow R-\overset{H}{\underset{|}{C}}=O + NH_3 + CO_2 + HX$

Nitrogen Oxidation:

4. $2NH_3 + 3\ HOX \rightarrow N_2 + 3\ HX + 3H_2O$

Self-Decomposition:

5. $HOX \rightarrow HX + \frac{1}{2}O_2$

6. $nHOX \rightarrow (n-1)\ HX + HXO_n$

Reactions with Organic Carbon

That organic carbon plays a major role in the fast decay processes seems inescapable. As seen in Figure 8, the rate of chlorine decay in an estuarine water sample can be significantly slowed if the sample is first subjected to ultrafiltration (Amicon UM 2) before chlorination. Analysis shows that the material removed by this treatment is mostly organic. The rate is more dramatically reduced if the sample is first passed through an XAD column to remove organic molecules. Eppley et al. (1976) reported that most of the fast decay in Southern California coastal water could be eliminated if the water was treated by a UV oxidation procedure to remove organic carbon prior to chlorination. Crane (personal communication, EPA Bears Bluff Field Station) has found an excellent correlation between water color (presumably a measure of dissolved humic compounds) and chlorine demand in a South Carolina estuary.

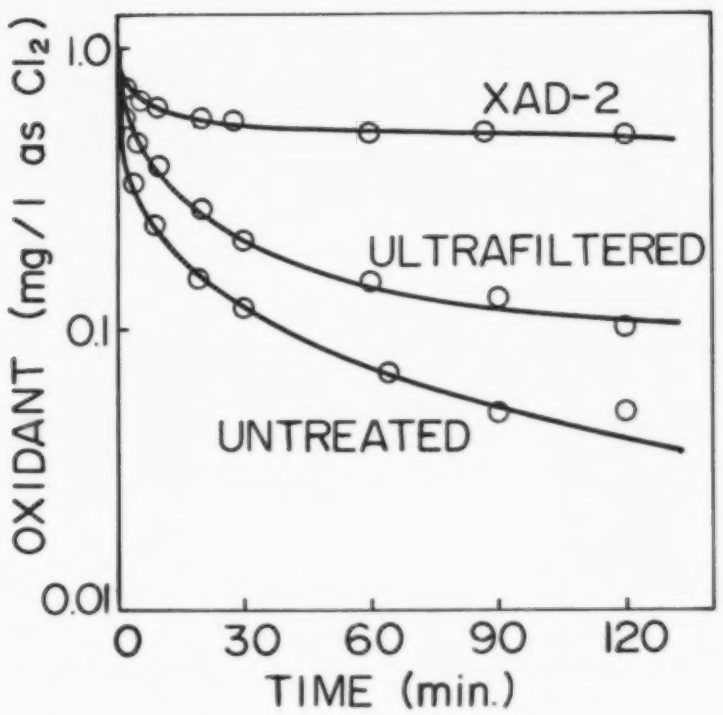


Figure 8. Effect of removing organic matter on decay. Ultrafiltration employed Amicon UM-2 membrane filters.

However, it is inconsistent to argue on the one hand, that oxidant is consumed mostly by reaction with organic carbon while also arguing that negligible haloform production occurred because of the rapid disappearance of oxidant. One way to resolve this conflict is to hypothesize that the combination of elevated temperature and intense agitation in the condensers increases the availability of reactive sites on the entrained organic flocs and particles. Thus, instead of getting multiple halogen substitution at relatively few carbon atoms, a necessary condition for haloform production, one gets single halogen substitution at many different carbon atoms. According to this hypothesis, the resulting halogenated macromolecules are relatively stable and fail to split-off low molecular weight fragments which would be detectable by methods based on gas chromatography.

Support for this hypothesis was obtained by isolating (by ultrafiltration) the macromolecular organic matter from samples collected within a few minutes of each other in the intake and the discharge canals at Chalk Point. The macromolecular matter was then analyzed, the halogens being determined by neutron activation analysis. The results (Table 5) indicate that both samples are very similar except for the bromine content in the sample from the discharge canal. We infer that this bromine is bound to the macromolecules as a result of chlorination. The data also show significant chlorine in both these samples, but we believe this is simply residual salt, rather than carbon-bound chlorine because it does not increase from the intake to the discharge canal.

TABLE 5. MACROMOLECULAR ORGANIC MATTER

Item	Intake Canal	Discharge Canal
C %	39.72	39.31
H %	5.80	6.18
N %	5.69	4.77
Cl %	0.81	0.85
Br %	0.04	1.60
I %	0.0030	0.0026
O + S(difference) %	47.94	47.29
	100.00	100.00
Ash %	6.40	6.42
C/N (molar)	8.14	9.61
Amount Recovered ($mg\ l^{-1}$)	1.31	1.29

Reactions with organic carbon, although undoubtedly important, can be over-emphasized. Other reactions listed in Table 4 probably are also important, especially in waters that contain very little organic carbon, but since these reactions are not directly relevant to the subject of this report, they will not be discussed here.

BACK RIVER WASTEWATER TREATMENT PLANT

When first encountered, the very low haloform yields at Chalk Point caused concern that perhaps haloforms were being produced, but were lost rapidly or masked by other components in the water. To evaluate this possibility, we decided to study a halocarbon source for which we would not have to depend upon halocarbon synthesis from chlorine. We chose a large sewage treatment plant located on the Back River estuary, east of Baltimore, Maryland, where we established that a suite of volatile halocarbons was present in the effluent even before chlorination. Thus, the vagaries of the halocarbon production process were eliminated from the experimental design.

Figure 9 is a map of Back River, a shallow, 12-km-long tributary estuary to the Chesapeake Bay with a salinity range of about 0.4 g/kg. Its mean depth is about 1 m and it is well mixed vertically. Near its upper end, Back River receives 1.5 to 1.9 x 10^8 l of wastewater/day from Baltimore's main sewage treatment plant; the waste discharges often exceed freshwater flow from the watershed by a factor of 2 (Helz et al., 1975). The plant provides 100% secondary treatment (mostly by the trickling filter process) to domestic and commercial wastes. The effluent is chlorinated before discharge.

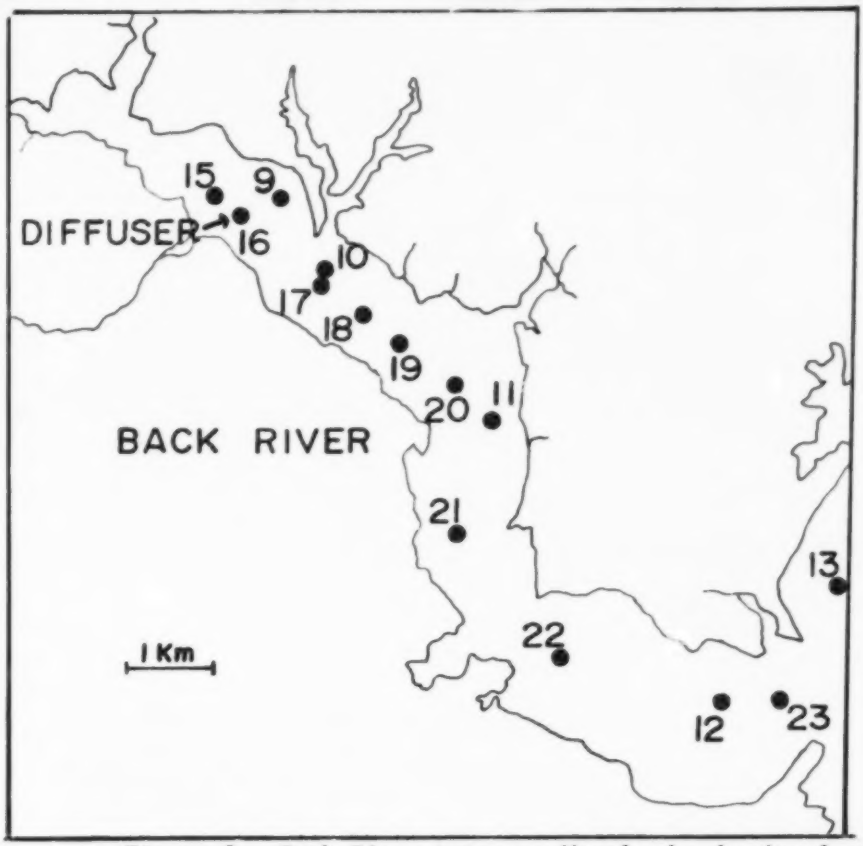


Figure 9. Back River estuary, Maryland, showing locations of sampling points. See Appendix A for latitudes and longitudes.

The first series of samples from Back River (Numbers 8 to 12) were collected in early February, 1977, after the northern Chesapeake Bay had been covered with ice for more than one month. The only uncovered area was a 0.2 km diameter patch of water immediately above the underwater diffusers at the discharge point in mid-river. The second set of samples (numbers 13 to 23) was collected in early May, 1977, six weeks after the spring thaw.

Results

The volatile halocarbons found in Back River (Table 6) are very different from those produced by chlorinating estuarine waters (Table 2). The Back River assemblage of compounds must be derived from the numerous commercial and light-industrial firms which the treatment plant serves.

Although the same assemblage of compounds was found in February and May, the amounts of each compound were much lower in the latter month. This difference may be due to a slower rate of halocarbon disposal into the sewage system in May or to an increased halocarbon volatilization rate during the trickling filter process. The first seems less likely because we know of no reason why the disposal rate should change drastically with season. The large differences between the February and May in-plant samples (8 and 14) are reflected by all the samples from the receiving waters; this rules out the possibility that the February in-plant sample was spurious because a halocarbon slug was passing by chance through the plant when the sample was taken.

TABLE 6. HALOCARBONS (μM) IN BACK RIVER

Sample[a]	Salinity	CH_2Cl_2	$CHCl_3$	CCl_4	CCl_2=CHCl	CCl_2=CCl_2
February 1977 (Ice cover):						
8[b]	-	775	413	186	230	369
9	0.57	512	330	97	113	356
10	0.69	304	238	60	88	337
11	1.42	152	207	57	50	114
12	2.92	ND	18	ND	2	5
13	3.16	ND	ND	ND	ND	ND
May 1977 (Open water):						
14[b]	-	47	106	14	106	50
15	0.34	ND	3	ND	4	ND
16	0.36	24	71	3	75	35
17	0.35	9	8	2	14	4
18	0.34	ND	1	ND	2	ND
19-23 No volatile halocarbons detected seaward of station 18.						

a. Sample numbers refer to Figure 10.
b. Samples 8 and 14 were taken in the treatment plant just before final chlorination.

In a seaward direction, the concentration of volatile halocarbons decreases systematically. The dominant process causing this decrease is simply tidal mixing of the effluent with saline Chesapeake Bay water. However, if dilution were the only process (i.e., if halocarbons mixed conservatively), then a plot of halocarbon concentration vs. specific conductance (measured at 25°C) would be linear (Boyle et al., 1974; Helz et al., 1975). However, such plots were non-linear in winter (Figure 10). Since Back River was almost entirely covered with ice, the non-conservative behavior cannot be ascribed to volatilization. When May samples were collected, there was not sufficient contrast between the specific conductance of the effluent and of the water off the mouth of Back River to allow these data to be treated as in Figure 10. However, it is probably significant that the seaward decline in halocarbon concentrations was much more abrupt in May. Values near or below the detection limit were encountered within 2 km of the outfall in May. In contrast, in the February series, values at station 12 (about 4 km from the outfall) were only 20-50% of the effluent values. More rapid loss in the later samples may be due either to volatilization in the absence of ice cover or possibly to more active biodegradation.

Discussion

Table 7 lists the major industrially produced, volatile halocarbons ranked according to rate of release to the environment. Release rates were determined by Nelson and Van Duuren (1975) by estimating for the United States the fraction of production plus imports used dispersively, plus the fraction of production lost during manufacture. Of the 11 compounds listed, three (CCl_2F_2, CCl_3F and CH_2Br-CH_2Br) would not be expected in wastewaters because they are released directly to the atmosphere. The two fluorocarbons are used mainly as refrigerants and aerosol propellants, and CH_2Br-CH_2Br is used mainly as a gasoline additive. A fourth compound, CH_2=CHCl (vinyl chloride), is probably too volatile to be retained in wastewater during treatment, even if it were somehow present initially. Of the remaining seven compounds in Table 7, five were found at the nM level in Back River. It is not known whether the other two, CH_2Cl-CH_2Cl and CH_3-CCl_3, are absent because they are not discharged into the sewage system in significant quantities, or because they are degraded or adsorbed from the wastewater before leaving the plant. Octanol-water partition coefficients, estimated by the method of Leo (1975), have been included in Table 7. These coefficients are considered a good measure of the lipophilic character of a compound and have been shown to correlate with the tendency of a compound to be bioactive and to bioaccumulate (Neely et al., 1974). However, neither of the two missing compounds in Table 7 is particularly distinctive with respect to its partition coefficient or to its volatility. Interestingly, no clear relationship exists between the partition coefficient and the degree of curvature in the concentration vs. salinity curves in Figure 10. CH_2Cl_2 (with the greatest curvature) and CCl_2=CCl_2 (with the least) have essentially the same partition coefficient.

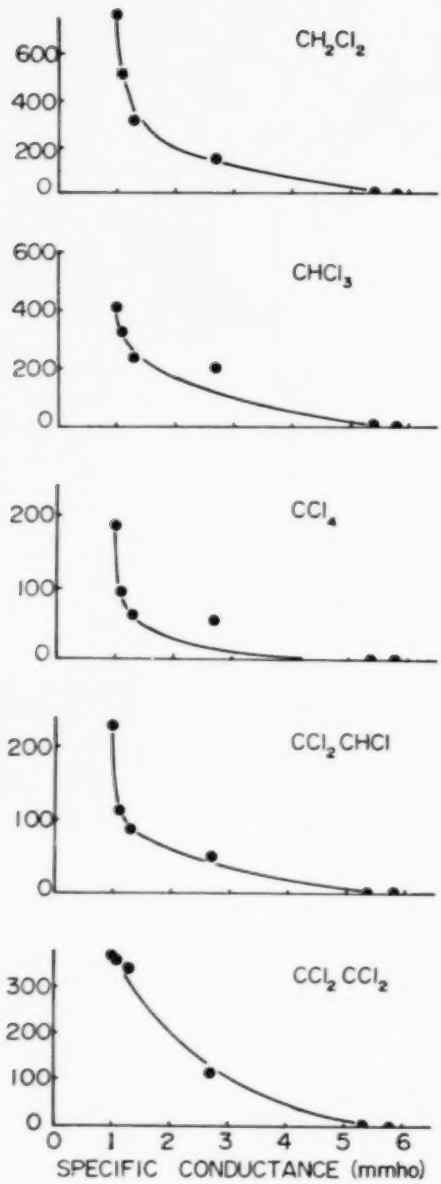


Figure 10. Halocarbon patterns in Back River. Vertical scales are all in nanomolar units for the indicated halocarbon.

TABLE 7: MAJOR INDUSTRIALLY PRODUCED HALOCARBONS RANKED BY RELEASE RATE

Compound	Release Rate (10^9 g yr^{-1})	Boiling Point (^oC)	log p_{oct}	In Back River
$CCl_2=CCl_2$	267	121	1.27	yes
CH_2Cl-CH_2Cl	245	83	1.48	no
$CHCl=CCl_2$	195	87	0.96	yes
CCl_2F_2	183	-28	2.08	no
CH_2Cl_2	167	40	1.26	yes
CH_2Br-CH_2Br	138	131	1.76	no
CH_3-CCl_3	129	74	2.50	no
CCl_3F	124	24	2.52	no
$CHCl_3$	76	61	1.96	yes
$CH_2=CHCl$	67	-14	0.34	no
CCl_4	48	77	2.96	yes

The much less rapid decrease in halocarbon concentrations when Back River was covered with ice suggests that volatilization is an important loss process. Dilling et al. (1975) and Dilling (1977) established that a large variety of C_1-C_3 halocarbons escape from open, stirred beakers in the laboratory with half lives (τ) on the order of 20 min. Liss and Slater (1974) have developed a simple model by which the rates of diffusive exchange of gases across the air-sea interface may be estimated. The model, as applied to the volatile halocarbons, leads to the following decay equation (Mackay and Leinonen, 1975):

$$C_t = C_o \exp(-K_1 t/L) \quad (4)$$

Here, C_o is the initial concentration, and C_t is the mean concentration at time=t_o; L is the mean depth of the water. Values of K_1 are presented in Table 8. The half-life of a compound in a well mixed water body would be:

$$\tau = 0.69\ L\ K_1^{-1} \quad (5)$$

Values of τ for two arbitrary mean depths are also given in Table 8. Because the validity of the simple Liss-Slater model may be subject to challenge, especially if applied to organic-rich, contaminated water around waste discharges, the half-lives in Table 8 must be regarded as tentative estimates. However, the important implication, that relatively shallow, well-mixed coastal waters will lose volatile halocarbons to the atmosphere within a few days, is probably correct.

It is noteworthy that the half-lives for all the compounds in Table 8 are similar in magnitude. This implies that although volatilization will cause fairly rapid decline in the concentration of any one compound, it will cause the concentration ratio between two compounds to change only slowly. Thus, these ratios could be "fingerprints" for a particular discharge plume and might be useful as plume tracers.

TABLE 8. LOSS RATES FOR VOLATILE HALOCARBONS

	K_1 (cm hr^{-1})	τ (hrs)	
		L = 1m	L = 5m
$CCl_2=CCl_2$	10.2	6.8	34
$CHCl=CCl_2$	11.3	5.9	30
CH_2Cl_2	13.1	5.3	26
CH_3CCl_3	11.4	6.0	30
$CHCl_3$	11.4	6.0	30
CCl_4	10.6	6.5	33
$CHBrCl_2$	8.9	7.8	39
$CHBr_2Cl$	6.8	10.2	51
$CHBr_3$	4.1	16.9	85

Loss of volatile halocarbons to the atmosphere is likely to constitute a permanent sink from the aquatic geochemist's viewpoint. Published estimates for the lifetime of these compounds in the troposphere range from a few days for the unsaturated compounds to a thousand years for CCl_4 (Yung et al., 1975; Dilling et al., 1976; Galbally, 1976). However, even in contaminated urban air, concentrations of these compounds are usually less than 1×10^{-9} by volume. Since the Henry's law constants (Dilling, 1977) are mostly less than unity, rain would contain much less than 1 nM, even if saturated. This is below the concentrations found in this study; therefore in contaminated coastal waters, rain will be a dilutent rather than a source. Measurements in rainwater by Pearson and McConnell (1975) support this conclusion.

Whereas dilution and volatilization are probably the major processes that control concentration patterns of volatile hydrocarbons in transport away from a discharge point, the February Back River data show that these compounds are consumed to some extent even when volatilization is precluded by ice cover. A number of processes might contribute to this. Hydrolysis or similar abiotic chemical mechanisms might be involved, although limited available information suggests that these processes will be slow. For example, Zafiriou (1975) estimated that the 50% conversion of CH_3Cl to CH_3OH in seawater would take 2.5 yr at 20°C and 14 yr at 10°C. Dilling et al. (1975) determined half lives of 9 to 18 months for 5 chlorocarbons in oxygenated solutions. Exposure of the solutions to sunlight increased the

decay rate by a factor of 1.5 to 2.0 for olefinic compounds, but had little effect on saturated compounds. The products in these reactions were not determined.

Whether biochemical pathways offer a faster consumption mechanism for volatile halocarbons is not yet clear. A brief attempt by Jensen and Rosenburg (1975) to answer this question yielded inconclusive results.

A potentially important removal mechanism in Back River involves transfer into the sediments. Although our results and those of others suggest that volatile halocarbons are inefficiently adsorbed by such substances as humic acid, ferric hydroxide, and clay (montmorillonite), there may be biologic pathways in which the compounds become bound in fecal pellets or other biogenic debris. Furthermore, the sediments in Back River have the consistency of black mayonnaise and may act somewhat like a non-polar liquid, simply extracting the dissolved halocarbons from the overlying aqueous layer. However, two attempts to establish the presence of these compounds in Back River sediments yielded negative results. In one experiment, 5 g of sediment was placed in a septum vial with 40 ml of H_2O; after sealing, the vial was shaken for an hour at 60°C, and the headspace above the slurry then analyzed. In the second experiment, a Soxhlet extraction of 50 g of sediment was performed for 1 week with 9:1 benzene-methanol. These experiments indicate that if volatile halocarbons are transferred into the Back River sediments, then they are probably degraded there, presumably by anaerobic biologic processes.

SECTION 5

OTHER ACTIVITIES

WORKSHOP

In the Spring of 1976, a workshop on the fate and effects of chlorine in Coastal Waters was held at Solomons, Maryland, with financial support from this grant. The workshop was organized jointly by the principal investigator and Dr. Ronald Block of the University of Maryland. About 30 scientists from as far away as Great Britain participated. Although there were 15 scheduled talks in the 2½ days of the workshop, emphasis was placed on informal discussion of problems and research needs associated with the use of chlorine in marine waters.

A full report on the workshop has been published (Chesapeake Science, 18, 96-160), and reprints of this report have been provided to EPA. Among the research needs identified in that report are a need to understand the reaction paths and mechanisms by which chlorine disappears in marine water, a need to account for all the products and a need to improve analytical procedures. Bioassay methodology was a major topic of discussion at the Workshop and some recommendations regarding the design of bioassays have been made in the report.

PUBLICATIONS

The following publications have resulted from work on this project:

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APPENDIX

LATITUDE AND LONGITUDE OF STATIONS

Station Number	Latitude	Longitude
1	38° 49' 40"	76° 42' 25"
2	39° 11' 40"	76° 16' 45"
3	38° 33' 15"	76° 25' 20"
4	38° 25' 25"	76° 35' 35"
5	38° 20' 00"	76° 20' 50"
6	38° 14' 50"	76° 7' 55"
7	38° 14' 50"	76° 7' 10"
8	39° 17' 45"	76° 29' 20"
9	39° 17' 50"	76° 28' 15"
10	39° 17' 25"	76° 27' 55"
11	39° 16' 20"	76° 26' 25"
12	39° 14' 40"	76° 24' 20"
13	39° 15' 35"	76° 23' 55"
14	39° 17' 45"	76° 29' 20"
15	39° 17' 45"	76° 28' 40"
16	39° 17' 30"	76° 28' 15"
17	39° 17' 10"	76° 27' 55"
18	39° 17' 00"	76° 27' 40"
19	39° 16' 50"	76° 27' 15"
20	39° 16' 25"	76° 26' 40"
21	39° 15' 35"	76° 26' 45"
22	39° 14' 45"	76° 25' 50"
23	39° 14' 45"	76° 24' 40"